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New one-pot methods for the synthesis of metallonium dications $[1,2\text{-}(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}Cp^*)Os]^{2+}$ and $[1,1'\text{-}(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2Os]^{2+}$ based on decamethylosmocene or its derivatives

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The reaction of Cp^*_2Os or $[Cp^*_2OsH]^+PF_6^-$ with oleum on heating or UV photolysis of Cp^*_2Os in oleum under an inert atmosphere afforded two metallonium dications, *viz.*, $[1,2\text{-}(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}Cp^*)Os]^{2+}$ and $[1,1'\text{-}(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2Os]^{2+}$. The structures of these dications were confirmed by the results of their alkoxylation. The $[Os(H)_2(Cp^*)_2]^{2+}$ and $[Os(H)(Cp^*)(C_5Me_4CH_2)]^{2+}$ dications were detected as intermediates in the above syntheses. All compounds were characterized by NMR spectroscopy. Calculations of the dications were carried out using the density functional theory (DFT).

Key words: decamethylosmocene, protonation, UV photolysis, metallocenylmethyl dications, alkoxylation, NMR spectra, quantum-chemical calculations.

Earlier, we have developed[1—3] multistep procedures for the synthesis of the metallonium monocations $[(\eta^5\text{-}Cp^*)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)M]^+$ as well as for the preparation of the homoannular and heteroannular dications $[1,2\text{-}(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}Cp^*)M]^{2+}$ and $[1,1'\text{-}(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2M]^{2+}$ (M = Fe, Ru, or Os) starting from the corresponding carbinols. In addition, one-pot procedures have been devised[4—6] for the synthesis of the monocations (M = Ru or Os) based on permethylmetallocenes. One-pot methods were also developed[7] for the generation of the metallonium dications of ruthenium $[1,2\text{-}(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}Cp^*)Ru]^{2+}$ and its heteroannular analog by the reaction of decamethylruthenocene with oleum at room temperature or by UV photolysis of a solution of metallocene in a CF_3SO_3H—oleum mixture (in a weight ratio of ~1 : 1). In the present study, we extended the one-pot method to the synthesis of Os-containing dications.

Results and Discussion

Based on decamethylosmocene (**1a**) or its derivatives, *viz.*, salts of the $[Os(H)(Cp^*)_2]^+PF_6^-$ (**2a**) and $[Os(C_5Me_4CH_2)(Cp^*)]^+BF_4^-$ (**3a**) monocations (hereinafter, the codes of all salts denote only the cation without regard for the anion), one-pot methods were developed for oxidation giving rise to the 1,2-homoannular dication $[M(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)(\eta^5\text{-}Cp^*)]^{2+}$ (**4a**, M = Os) and the 1,1´-heteroannular dication $[M(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$ (**5a**, M = Os). The reactions of the starting osmium complexes **1a**—**3a** with oleum, CF_3SO_3H, and a CF_3SO_3H—oleum mixture (at various ratios) were studied and the influence of the solvent (CD_2Cl_2) on the course of the reactions was revealed. Dications **4a** and **5a** were synthesized also by UV photolysis of osmocene **1a** in oleum. The reactions were carried out according to procedures developed earlier.[6,7]

It was demonstrated that dications **4a** and **5a** can be prepared by keeping osmocene **1a** or its monohydride **2a** in 40% oleum at 50 °C for 2—3 h (Table 1, runs *3* and *20*). Dications **4a** and **5a** were also generated as the major products by UV photolysis of a solution of osmocene **1a** in oleum for 20 h (runs *4*—*6*). An analogous result can be obtained at room temperature by the reaction of oleum with monocation **3a** (run *23*).

The reaction of osmocene **1a** with CF_3SO_3H followed by UV photolysis of the reaction mixture (see Table 1, runs *7*—*9*) also afforded dications **4a** and **5a**. However, it is not an efficient procedure for their synthesis. The use of a CF_3SO_3H—oleum mixture (2.7 : 1) instead of CF_3SO_3H (runs *10*—*12*) was inefficient as well.

It should be noted that a change in the reaction conditions leads to a change in the ratio between the products. In oleum, dications **4a** and **5a** were generated in a ratio

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† Deceased.

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Table 1. Reactions of Cp^*_2Os (**1a**), $[Cp^*_2OsH]^+PF_6^-$ (**2a**), and $[Cp^*OsC_5Me_4CH_2]^+BF_4^-$ (**3a**) with acids under various conditions (photolysis, thermolysis)

Starting compound	Run	Medium	Reaction conditions, photolysis (*h*ν), T/°C, t	Percentage of complexes (%)						Ratio **4a** : **5a**
				3a	**4a**	**5a**	**6**	**7**	**9**	
1a	*1*[a]	Oleum	20[b]	—	15	12	—	54	—	1.22
	2	*Ditto*	20, 8 days	—	50	42	—	8	—	1.23
	3	»	50, 2 h	—	45	46	—	9	—	0.99
	4[a]	»	20[b]	—	21	20	—	47	6	1.06
	5	»	*h*ν, 35, 8 h	—	38	40	—	10	12	0.94
	6	»	*h*ν, 35, 20 h	—	44	45	—	—	11	0.98
	7	CF_3SO_3H	20[b]	—	—	—	100	—	—	—
	8	*Ditto*	*h*ν, 35, 5 h	5	8	5	1	81	—	1.52
	9[c]	»	*h*ν, 35, 25 h	5	11	7	—	73	4	1.47
	10[d]	CF_3SO_3H, oleum	20[b]	—	17	11	—	68	4	1.41
	11	*Ditto*	*h*ν, 35, 10 h	—	23	19	—	49	9	1.19
	12	»	*h*ν, 35, 20 h	—	26	23	—	39	12	1.14
	13[e]	CF_3SO_3H, oleum, CD_2Cl_2	20[b]	<1	4	3	87	6	—	1.34
	14	*Ditto*	20, 8 days	5	7	5	60	23	—	1.29
	15	»	20, 23 days	12	21	12	4	51	—	1.83
	16	»	20, 28 days	34	22	15	—	29	—	1.48
	17	»	20, 36 days	13	43	35	—	—	9	1.24
2a	*18*[a]	Oleum	20[b]	—	28	31	12	25	—	1.11
	19[a]	*Ditto*	50, 2 h	—	42	41	—	—	7	1.05
	20	»	50, 3 h	—	45	47	—	—	8	0.96
	21	CF_3SO_3H	20[b]	—	5	3	89	3	—	1.62
3a	*22*[a]	Oleum (20%)	20[b]	—	21	19	—	48	—	1.11
	23	Oleum	20[b]	—	49	51	—	—	—	0.94

[a] Paramagnetic compound **8** was present in a solution; in runs: *1*, 19%; *4*, 6%; *18*, 4%; *19*, 10%; *22*, 12%.

[b] The composition of the reaction mixture after mixing of the reagents.

[c] An increase in the irradiation time to 40 h led to only a slight change in the ratio between the reaction products. In this case, the percentage of **7** was 67%.

[d] The weight ratio CF_3SO_3H : 40% oleum = 2.7 : 1.

[e] The weight ratio CF_3SO_3H : 40% oleum = 1 : 2; the weight of CD_2Cl_2 was 0.1275 g.

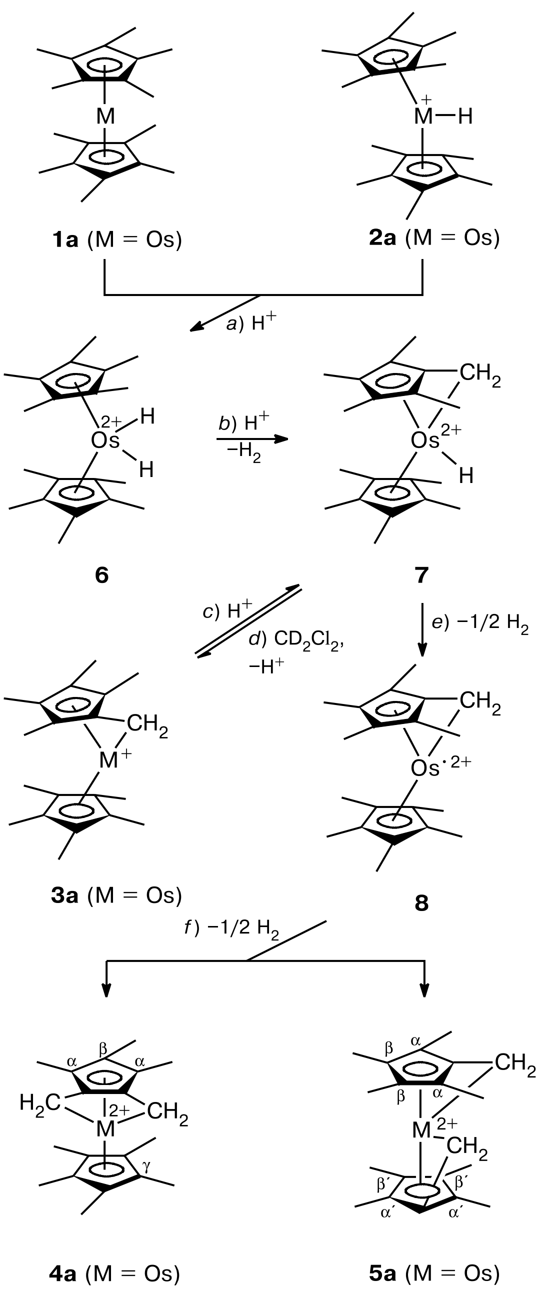
close to unity (0.94—1.23), whereas this ratio in the reaction with the use of CF_3SO_3H was ~1.5 (1.47—1.62).

The $[Os(H)_2(Cp^*)_2]^{2+}$ (**6**) and $[Os(H)(Cp^*)(C_5Me_4CH_2)]^{2+}$ dications (**7** is protonated cation **3a**) were identified as intermediates in the reactions with acids. Dication **6** is a product of the reaction of osmocene **1a** with CF_3SO_3H★ (see Table 1, runs *7*, *13*, and *14*) as well as of the reaction of monohydride **2a** with oleum (run *18*) or CF_3SO_3H (run *21*). Dication **7** was detected not only upon protonation of monocation **3a** (run *22*) but also in all reactions of osmocene **1a** or monocation **2a** with acids (runs *1—5*, *8*, *9*, *18*, and *21*).

The reaction of osmocene **1a** with a CF_3SO_3H—oleum mixture (1 : 2) (runs *13—17*) in the presence of CD_2Cl_2 as the solvent afforded the above-mentioned products along with monocation **3a**. In runs *13—16*, the amount of the latter gradually increased and then decreased (run *17*). A comparison of runs *15* and *16* shows that the percentage of dication **7** decreased from 51 to 29%, the percentage of monocation **3a** increased, whereas the percentages of dications **4a** and **5a** in the mixture remained unchanged. In the experiments carried out in the absence of the solvent (runs *10—12*), the formation of monocation **3a** was not observed. Hence, it can be concluded that monocation **3a** is most probably generated from dication **7**, and CD_2Cl_2 serves in this reaction as a deprotonating reagent (Scheme 1, step *d*). Earlier, we have observed[6] deprotonation giving rise to Cp^*_2Os upon irradiation of $[Cp^*_2OsH]^+An^-$ in CD_2Cl_2. Protonation—deprotonation of the metal atom in half-sandwich Ru complexes in a CF_3SO_3H/CD_2Cl_2 medium have also been described in the study.[8]

★ The formation of either $[Os(H)(Cp^*)_2]^+An^-$ (**2a**) or $[Os(H)_2(Cp^*)_2]^{2+} \cdot 2An^-$ (**6**) (An^- is the anion) by the reaction of $Os(Cp^*)_2$ (**1a**) with CF_3SO_3H depends on the strength of acid; the acid from the freshly opened tube gave dihydride **6**.

Scheme 1



It should be emphasized that the reactions in oleum afforded a paramagnetic compound, as evidenced by the presence of a broad ($\Delta\nu_{1/2} \approx$ 182 Hz) high-field signal (δ = −20.45) in the ^{1}H NMR spectra of the reaction mixtures. Taking into account that this signal was absent in the spectra of the final reaction products and was manifested in the reactions not only with the use of osmocene **1a** (see Table 1, runs *1* and *4*) or monohydride **2a** (runs *18* and *19*) as the starting compound but also with the use of monocation **3a** (run *22*), it can be hypothesized that the $[Os(Cp^*)(C_5Me_4CH_2)]^{\cdot 2+}$ radical cation (**8**) was formed as an intermediate. In addition, the $[(1,2\text{-}(CH_2)_2C_5Me_3)Os(1'\text{-}CH_2C_5Me_4)]^{3+}$ trication (**9**) was detected[9] in some reactions (see Table 1, runs *4—6*, *9—12*, *17*, *19*, and *20*).

With the aim of studying the chemical transformations of dications **4a** and **5a** synthesized in acidic media and confirming their structures, we carried out alkoxylation with NaOMe. A mixture of dications **4a** (45%) and **5a** (46%), which was prepared analogously to run *3* (see Table 1), was treated with NaOMe in MeOH. [1,2-Di(methoxymethyl)trimethylcyclopentadienyl](pentamethylcyclopentadienyl)osmium (**10**) (42%) and bis(methoxymethyltetramethylcyclopentadienyl)osmium (**11**) (58%) were isolated from an ethereal extract of an alkaline solution (Scheme 2). The total yield of diethers **10** and **11** was 78%.

Scheme 2

$[Os(\eta^5\text{-}Cp^*)(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)]^{2+}$ +
4a
+ $[Os(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$ + NaOMe/MeOH $\longrightarrow$
5a
$\longrightarrow$ $Os(Cp^*)[C_5Me_3(CH_2OMe)_2]$ + $Os(C_5Me_4CH_2OMe)_2$
10 **11**

For comparison, we also subjected the salt of monocation **3a** (An^- = BF_4^-) to alkoxylation by NaOMe. Monoether **12** was prepared in 84% yield (Scheme 3).

Scheme 3

$[Os(\eta^5\text{-}Cp^*)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)]^+BF_4^-$ + NaOMe $\longrightarrow$
3a
$\longrightarrow$ $Os(Cp^*)(C_5Me_4CH_2OMe)$
12

Osmium complexes **3a—5a**, **6**, **7**, and **9** synthesized in solutions of acids were characterized by ^{1}H NMR (Table 2) and ^{13}C NMR spectroscopy (Table 3). Previously unknown monoether **12** and diethers **10** and **11** were identified based on the ^{1}H NMR (Table 4) and mass spectra. Ethers **10—12** were characterized by ^{13}C NMR spectra. Monoether **12** was additionally characterized by elemental analysis (see the Experimental section). We failed to obtain reliable elemental analysis data for isomeric diethers **10** and **11** because these compounds, although being rather stable in solutions, are unstable in the individual form.

The ^{1}H NMR spectrum of monohydride **2a** in CD_2Cl_2 is identical with that published in the literature.[6] The ^{1}H NMR spectrum of dihydride dication **6** has two singlets, both signals being shifted downfield compared to those in the spectrum of **2a**; the ratio between these sig-

Table 2. ^{1}H NMR spectroscopic data for osmium complexes **2a—5a**, **6**, and **7** in various media

Complex	Medium	δ					
		OsH	C_5Me_5	$C_5Me_n(CH_2)_{5-n}$			
				α,α′-Me	β,β′-Me	CH_2^{AB}	$\Delta\delta_{AB}$ ($^2J_{H,H}$/Hz)
2a[a]	CD_2Cl_2	−15.64	1.96	—	—	—	—
3a[a]	CF_3SO_3H	—	2.05	1.77	2.03	4.59	—
	CF_3SO_3H, oleum, CD_2Cl_2	—	1.91	1.59	1.85	4.38	—
4a	CF_3SO_3H	—	2.48	2.08	2.46	4.80, 5.41	0.61 (J = 2.5)
	Oleum	—	2.47	2.04	2.46	4.83, 5.39	0.56
	CF_3SO_3H, oleum[b]	—	2.41	1.97	2.41	4.75, 5.35	0.60
	CF_3SO_3H, oleum, CD_2Cl_2	—	2.29	1.85	2.28	4.65, 5.21	0.56
	Oleum, CD_2Cl_2	—	2.28	1.84	2.26	4.63, 5.19	0.56
4a[c]	CF_3SO_3H, CD_2Cl_2, CD_3NO_2	—	2.25	1.80	2.25	4.79, 5.37	0.58
5a	CF_3SO_3H	—	—	2.09, 2.22	2.31, 2.75	5.33, 5.77	0.44 (J = 1.2)
	Oleum	—	—	2.08, 2.21	2.30, 2.74	5.32, 5.78	0.46
	CF_3SO_3H, oleum[b]	—	—	2.02, 2.15	2.24, 2.67	5.27, 5.71	0.44
	CF_3SO_3H, oleum, CD_2Cl_2	—	—	1.90, 2.03	2.12, 2.56	5.15, 5.60	0.45
	Oleum, CD_2Cl_2	—	—	1.89, 2.01	2.10, 2.55	5.13, 5.58	0.45
5a[c]	CF_3SO_3H, CD_2Cl_2, CD_3NO_2	—	—	1.82, 1.99	2.09, 2.51	5.28, 5.74	0.46
6	CF_3SO_3H	−14.62	2.63	—	—	—	—
	Oleum	−14.87	2.39	—	—	—	—
	CF_3SO_3H, oleum, CD_2Cl_2	−14.75	2.46	—	—	—	—
7	CF_3SO_3H	−15.44	2.54	2.14, 2.28	2.48, 2.94	5.14, 5.75	0.61
	Oleum	−15.36	2.51	2.12, 2.24	2.43, 2.93	5.07, 5.72	0.65
	CF_3SO_3H, oleum	−15.46	2.46	2.06, 2.20	2.40, 2.87	5.06, 5.68	0.62
	CF_3SO_3H, oleum, CD_2Cl_2	−15.51	2.38	1.94, 2.12	2.34, 2.80	4.97, 5.60	0.63
	Oleum, CD_2Cl_2	−15.51	2.35	1.95, 2.08	2.28, 2.77	4.92, 5.57	0.65

[a] *Cf.* lit. data.[6]

[b] Oleum, 0.319 g; CF_3SO_3H, 1.48 mmol; 20 °C, 8 days.

[c] Published data.[10]

nals is 15 : 1. The spectra of dications **4a** and **5a** are identical with those published in the literature.[10] The same is true for the spectrum of monocation **3a**.[6] The spectra of compounds **3a—5a** depend on the solvents used. All signals of dication **7** are broadened: $\Delta\nu_{1/2} \approx$ 19.5—21.0 Hz for the signals of the Me groups of the C_5Me_4 ring and the CH_2 group, $\Delta\nu_{1/2} \approx$ 5—6 and 2.6—3.9 Hz for the signals of OsH and the Cp* ring, respectively. The protons of the CH_2 group in dication **7**, like those in $[(Cp^*)Re(H)(C_5Me_4CH_2)]^+$,[11] are nonequivalent. The protons of the Me groups of the $C_5Me_4CH_2$ ring are also nonequivalent (four signals, 3 H each). This is indicative of the absence of the symmetry plane in the conformer of dication **7** that formed.

Table 3. ^{13}C NMR spectroscopic data for osmium complexes **2a—5a**, **6**, and **7**

Complex	Medium	δ ($^1J_{C,H}$/Hz)							
		CH_2	α-Me, α´-Me	β-Me, β´-Me	γ-Me	C atoms of Cp* rings			
						C(1)	C_α, $C_{\alpha'}$	C_β, $C_{\beta'}$	C_γ
2a	CH_2Cl_2	—	—	—	9.35	—	—	—	90.91
4a[a]	CF_3SO_3H, oleum	70.92 (J = 171)	9.41 (2 C)	10.23 (1 C)	10.0	134.66	105.53	115.06	107.58
5a	CF_3SO_3H, oleum	73.65 (J = 170)	7.32, 9.18	9.43, 11.39	—	100.29[b]	106.28,[b] 112.13[b]	116.60,[b] 117.11[b]	—
6	CF_3SO_3H	—	—	—	8.77	—	—	—	106.32
7	Oleum	66.50	8.55, 8.58	9.35 (2 C)	9.29	107.06	96.39, 102.74	108.40 (2 C)	105.53

[a] *Cf.* lit. data.[2]

[b] The assignment to particular columns is tentative.

Earlier,[10] it has been demonstrated that only the *gauche* conformer (φ = 90°) occurs for heteroannular dication **5a**. As can be seen from Table 2, $\Delta\delta_{AB}$ = 0.44—0.46 for the *gauche* conformer of dication **5a**, whereas $\Delta\delta_{AB}$ = 0.61—0.65 for dication **7**. An increase in $\Delta\delta_{AB}$ is, apparently, associated not only with the presence of the substituent at the metal atom but also with an increase in the angle φ ($\varphi \geq 90°$) in the conformer of **7** that formed.

The formation of trication **9** was judged from three signals of the protons of the CH_2 groups with equal intensities (2 H each) at δ 4.5—5.5 (δ: in oleum, 4.71 d, 5.28 d, and 5.15 s; in CF_3SO_3H, 5.00 d, 5.63 d, and 5.47 s) (*cf.* lit. data[9]).

The ^{13}C NMR spectroscopic data (see Table 3) for the compounds synthesized also confirmed their structures. The spectra of monohydride **2a** and dihydride **6** have two signals each, the signal of the C_γ atoms of dihydride **6** being shifted downfield compared to the analogous signal for monohydride **2a**. The spectrum of dication **4a** is identical with that published in the literature.[2] In the ^{13}C NMR spectrum of dication **5a**, the atoms of two CH_2 groups have equal chemical shifts (δ 73.65) and are observed as one triplet with $^1J_{C,H}$ = 170 Hz in the spectrum measured without suppression of C—H coupling. The methyl groups of dication **5a** give four signals (α, α´, β, β´; 2 C each; for notations, see Scheme 1), the chemical shift of the C_β and $C_{\beta'}$ atoms of the Me groups being larger than that of the C_α and $C_{\alpha'}$ atoms. The same situation is observed for four pairs of the C atoms of two $\underline{C}_5Me_4$ rings. The ^{13}C NMR spectrum has five signals of the C atoms of the $\underline{C}_5Me_4$ rings with equal integral intensities (2 C(1), 2 C_α, 2 $C_{\alpha'}$, 2 C_β, and 2 $C_{\beta'}$) and, hence, it was impossible to make the unambiguous assignment (see Table 3). In the ^{13}C NMR spectrum of dication **7**, the signal of the C atom of the CH_2 group (δ 66.50) is shifted downfield compared to the analogous signal for monocation **3a** (δ_{CH_2} 55.36),[2] which is indicative of an increase in the charge on the Os atom. Four nonequivalent Me groups give three signals (α-Me (1 C), α-Me (1 C), and β-Me (2 C)) analogously to the C atoms of the $\underline{C}_5Me_4$ ring (which also give three signals).

Table 4. ^{1}H NMR spectroscopic data for osmium complexes **10—12**

Complex	δ				
	α-Me	β-Me	γ-Me	CH_2O	OMe
10	1.90 (s, 6 H)	1.67 (s, 3 H)	1.75 (s, 15 H)	3.98, 4.10 (dd, AB system, $^2J_{H,H}$ = 11.6 Hz)	3.42 (s, 6 H)
11	1.89 (s, 12 H)	1.71 (s, 12 H)	—	3.99 (s, 4 H)	3.33 (s, 6 H)
12	1.91 (s, 6 H)	1.74 (s, 6 H)	1.77 (s, 15 H)	4.02 (s, 2 H)	3.36 (s, 3 H)

The assignments of the signals of the protons of the α- and β-Me groups in the ^{1}H NMR spectra of neutral compounds **11** and **12** (see Table 4) were made based on the integral intensities of the signals of these protons in the spectrum of diether **10** ($\delta_{\alpha\text{-Me}} > \delta_{\beta\text{-Me}}$). The protons of two CH_2O groups in diether **10**, like the protons of two CH_2 groups in dication **4a**, are nonequivalent and are observed in the spectrum as signals of an AB system. In the spectrum of diether **11**, the methyl protons give two singlets (12 H each), although the protons of the Me groups in the ^{1}H NMR spectrum of dication **5a** are observed as four singlets of the α,α´-Me and β,β´-Me groups. Presumably, diether **11** adopts either the *syn* or *anti* conformation, both conformations having the symmetry plane.

In the ^{13}C NMR spectra of diethers **10** and **11** and monoether **12** (see the Experimental section), the signals of the C atoms of the CH_2O groups are observed at δ 68.04—68.75 (for EtOMe, at δ_{CH_2O} 68.9)[12] and the signals of the OMe groups are observed at δ 57.15—57.96 (δ_{OMe} 58.8).[12] The relationship between the chemical shifts of the C atoms of the α-Me and β-Me groups in diether **10** is analogous to that observed in the ^{1}H NMR spectra: $\delta_{\alpha\text{-Me}} > \delta_{\beta\text{-Me}}$. The ^{13}C NMR spectrum of diether **11**, like the ^{1}H NMR spectrum, is indicative of the *anti* conformation, because the C atoms of the α,α´- and β,β´-Me groups, like the C atoms of two rings, are manifested as two singlets at δ 11.20, 11.49 and 78.93, 79.45.

Earlier,[6] we have demonstrated that cationic hydrides $[Cp^*{}_2MH]^+$ (protonated metallocenes) and the metallocenium radical cations $[Cp^*{}_2M]^{\cdot +}$ are intermediates in the synthesis of the $[M(C_5Me_4CH_2)(Cp^*)]^+$ monocations (M = Os (**3a**), Ru (**3b**)) from decamethylmetallocenes $Cp_2{}^*M$ (M = Os (**1a**), Ru (**1b**)) in acidic media. Taking into account these facts, we propose a scheme of formation of dications **4a** and **5a** (see Scheme 1).

It should be noted that monocation **3a** was transformed into dications **4a** and **5a** (path *c—e—f*) (see Table 1, run *23*) without heating, *i.e.*, this transformation proceeded more readily than the transformation of osmocene **1a** or monohydride **2a** to dications **4a** and **5a** (path *a—b—e—f*), which required longer time and heating.

Oxidation of decamethylmetallocenes **1a** and **1b** [7] to the dications in strongly acidic media proceeded somewhat differently depending on the nature of metal. These differences are manifested both in changes in the reaction rate and the structures of intermediates and final products. In the presence of CF_3SO_3H, ruthenocene **1b** formed monohydride $[Ru(H)(Cp^*)_2]^+$ (**2b**),[6] whereas osmocene **1a** gave (as evidenced by the results of the present study) dihydride **6** under the same reaction conditions. This is indicative of an increase in the basicity of metallocenes in the series Fe < Ru < Os, which has been found earlier.[13]

In addition, it should be noted that osmocene **1a** gave dications **4a** and **5a**, whose structures are identical with those of the dications derived from the corresponding diols,[10] whereas ruthenocene **1b** produced the 1,2-homoannular dication $[Ru(\eta^5\text{-}Cp^*)(\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2)]^{2+}$ (**4b**), which is structurally similar to osmium dication **4a**, and the 1,1´-heteroannular dication, which differs from osmium analog **5a** and the $[Ru(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)_2]^{2+}$ dication (**5b**) synthesized from the corresponding diol $Ru(C_5Me_4CH_2OH)_2$. Based on the available data, it was assumed that this dication has the structure of $[Ru(\eta^2\text{-}H_2)(\eta^3{:}\sigma\text{-}C_5Me_4CH_2)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)]^{2+}$ (**5c**).[7]

The rate of the reaction of osmocene **1a** with oleum giving rise to dications **4** and **5** differs from that of the corresponding reaction of ruthenocene **1b**. For comparison, we carried out the reactions of osmocene **1a** and ruthenocene **1b** with 40% oleum under the same conditions at room temperature (~20 °C). As in the earlier study,[7] ruthenocene **1b** (17 μmol) was completely transformed into dications **4b** and **5c** (in a ratio of 0.87) in the reaction with oleum (0.63 g). Under the same conditions, the reaction of osmocene **1a** (17 μmol) with oleum (0.62 g) (see Table 1, run *4*) afforded a mixture of products containing only 41% of dications **4a** and **5a** (in a ratio of 1.06). It took 8 days to achieve the virtually complete (92%) conversion of osmocene **1a** into dications **4a** and **5a** at ~20 °C (see Table 1, runs *1* and *2*). Therefore, these experiments demonstrated that oxidation of ruthenocene **1b** with oleum giving rise to dications **4** and **5** proceeded more rapidly than oxidation of its osmium analog **1a**.

The observed difference in the structures of 1,1´-heteroannular osmium dication **5a** and ruthenium dication **5c** derived from the $[M(\eta^5\text{-}Cp^*)(\eta^5{:}\sigma\text{-}C_5Me_4CH_2)]^+$ monocations (**3a,b**) is, apparently, associated with the difference in the structure of the intermediates. Thus, the $[Os(H)(Cp^*)(C_5Me_4CH_2)]^{2+}$ dictation (**7**), which is a protonation product of monocation **3a**, was detected as the intermediate in oxidation of monocation **3a** to dications **4a** and **5a**. By contrast, an intermediate devoid of hydride hydrogen was observed upon photolysis of ruthenocene **1b** in a CF_3SO_3H—oleum mixture (7 : 1)[7] to form dications **4b** and **5c**. The ^{1}H NMR spectrum of this intermediate is analogous to that of monocation **3b**, which has broadened signals. We studied UV photolysis of monocation **3b** ($An^- = BF_4{}^-$) in CF_3SO_3H without the addition of oleum, *i.e.*, under the conditions that exclude the formation of dications. In the latter case, we also observed the formation of an analogous intermediate. The ^{1}H NMR spectra of the reaction mixtures obtained upon UV irradiation for 15 and 20 h (Fig. 1, *a*, *b*) have a signal of the protons of the α-Me groups (δ 1.64) of monocation **3b** along with broadened signals of intermediate **3c** (a signal of the protons of its α-Me groups is shifted downfield by Δδ 0.09), the signal of hydride hydrogen being absent. Intermediate **3c** was obtained as the major product (it comprised 85% of the reaction mixture) upon irradiation for 32 h (see Fig. 1, *c*). This experimented showed that the positively charged Ru atom in monocation **3b**, unlike the metal atom in Os-containing analog **3a**, was not protonated. In the ^{1}H NMR spectrum of intermediate **3c** (see Fig. 1, *c*), the signals of the α-Me, γ-Me, and CH_2 groups are most substantially broadened ($\Delta\nu_{1/2}$ = 16, 17.2, and 10.5 Hz, respectively) compared to the signals of the β-Me groups ($\Delta\nu_{1/2}$ = 3.1 Hz), which provides evidence that dynamic protonation—deprotonation processes took place. This suggests that the α-Me and γ-Me groups in monocation **3b** are most probably subjected to the attack of the proton (formation of methonium cations), which is consistent with the assumption made earlier.[7]

To confirm the structures of the homo- and heteroannular dications, we have carried out[14] quantum-chemi-

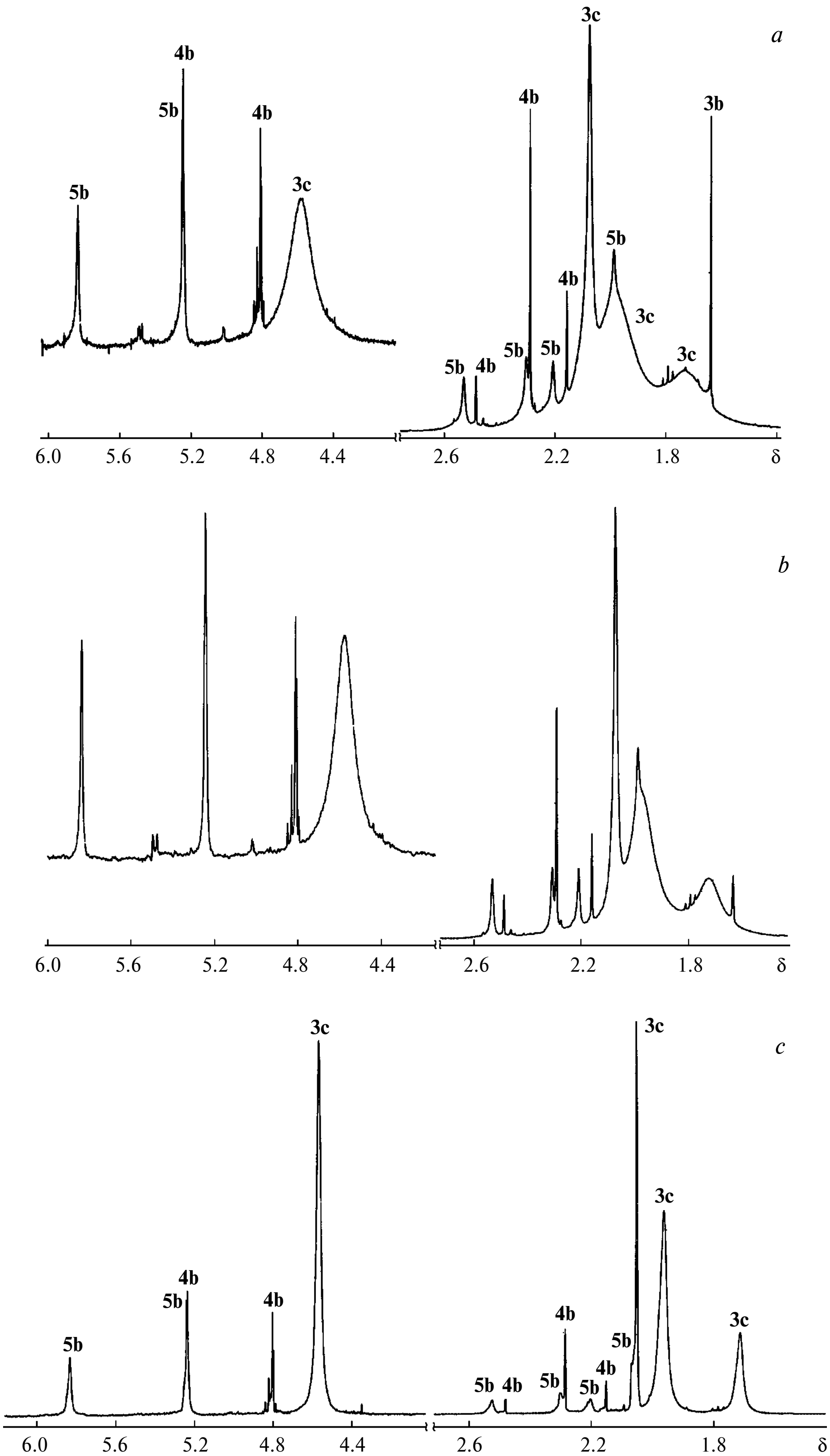
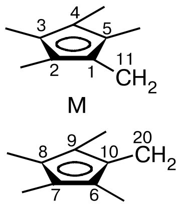


Fig. 1. ^{1}H NMR spectra used for monitoring of UV irradiation of a solution of the $[\mathrm{RuCp^*(C_5Me_4CH_2)}]^+\mathrm{BF_4}^-$ monocation (**3b**) in $\mathrm{CF_3SO_3H}$; *h*ν = 15 (*a*), 20 (*b*), and 32 h (*c*).

cal calculations for the Os (**4a**) and Ru (**4b** and **5b**) dications using the density functional theory (DFT). As part of our continuing studies, we carried out calculations for the *gauche* and *anti* conformations of heteroannular osmium dication **5a** analogous to ruthenium dication **5b**. The calculated geometric parameters and total energies of dications **5a,b** in the gas phase are given in Table 5. The atomic numbering scheme is analogous to that used earlier[14] for ruthenium dication **5b**. Calculations demonstrated that the energies of the *syn*, *gauche*, and *anti* conformers of Os-containing dication **5a** converged to one minimum corresponding to the *gauche* conformation, *i.e.*, neither the *syn* conformation nor the *anti* conformation occurs for dication **5a**. For Ru-containing analog **5b**, all three conformations exist, the *gauche* conformer being characterized by the minimum energy.[14] Earlier,[10] the structures of dications **5a,b** were calculated at the extended Hückel theory (EHT) level. It has been demonstrated[10] that for both these dications, the *gauche* conformation is energetically most favorable of three possible conformations (*syn, gauche*, and *anti*). It should also be noted that, according to calculations at the EHT level,[2] $\Delta E = E_{anti} - E_{gauche}$ are 15.5 and 9.4 kcal mol^{-1} for **5b** and **5a**, respectively, *i.e.*, **5b** is characterized by a deeper energy minimum than **5a**. The results of the present study and the data published earlier[7] provide unambiguous evidence that dications **5a,b** adopt the *gauche* conformation in solutions of acids. As can be seen from Table 5, osmium dication **5a** in the gas phase has a symmetrical structure, which was not observed for ruthenium dication **5b**.[14] For example, the M—C(11) and M—C(20) bond lengths in the *gauche* isomer of **5b** are 2.586 and 2.547 Å, respectively, whereas these bond lengths in the *gauche* isomer of **5a** have equal values (2.441 Å). An analogous situation is observed for the M—C(1) and M—C(10) bond lengths. In *gauche*-**5b**, these bonds differ in the length (2.194 and 2.187 Å), whereas these bond lengths in *gauche*-**5a** are equal (2.180 Å). In the homoannular dications,[14] the M—CH$_2$ distances are 2.395, 2.401 (**4a**) and 2.456, 2.456 Å (**4b**), respectively. At the same time, the ^{13}C NMR spectra indicate that both compounds **5a**,**b** and compounds **4a**,**b** in solutions have symmetrical structures because the CH$_2$ groups are manifested as one triplet for all four dications[7] (see Table 3). This difference is, apparently, attributed to the difference in the structures of the dications in the gas phase (DFT calculations) and the liquid state (NMR spectroscopy). Earlier, we have observed analogous differences in the study[15] of the structures of the [η^7-1,2-(CH$_2$)$_2$C$_5$Me$_3$MC$_5$Me$_4$CH$_2$-1′-η^6]$^{3+}$ trications (M = Os (**9a**), Ru (**9b**)) by the DFT method and NMR spectroscopy. In addition, it has been demonstrated[14] that there are particular differences in the M—CH$_2$ group bond lengths in monocations **3a,b** in the gas phase (DFT) and crystals (X-ray diffraction analysis).

Table 5. Bond lengths (*d*), bond angles (ω), and total energies (E_{tot}) for different conformers of the heteroannular osmium (**5a**) and ruthenium (**5b**) dications



5a,b

Parameter	*gauche*-**5a**[a]	*anti*-**5b**	*gauche*-**5b**	*syn*-**5b**
Bond		*d*/Å		
M—C(1)	2.180	2.189	2.194	2.192
M—C(2)	2.298	2.355	2.293	2.354
M—C(3)	2.425	2.535	2.427	2.422
M—C(4)	2.463	2.521	2.475	2.432
M—C(5)	2.350	2.321	2.365	2.358
M—C(6)	2.351	2.513	2.350	2.176
M—C(7)	2.465	2.501	2.453	2.359
M—C(8)	2.421	2.329	2.416	2.464
M—C(9)	2.296	2.181	2.293	2.429
M—C(10)	2.180	2.324	2.187	2.328
M—C(11)	2.441	2.515	2.586	2.687
M—C(16)	—	—	—	2.619
M—C(19)	—	2.482	—	—
M—C(20)	2.441	—	2.547	—
C(1)—C(2)	1.498	1.499	1.494	1.497
C(1)—C(5)	1.504	1.491	1.501	1.498
C(1)—C(11)	1.429	1.414	1.408	1.412
C(2)—C(3)	1.460	1.450	1.458	1.445
C(2)—C(12)	1.511	1.513	1.510	1.509
C(3)—C(4)	1.482	1.468	1.476	1.493
C(4)—C(5)	1.450	1.465	1.447	1.443
C(6)—C(7)	1.450	1.467	1.449	1.498
C(6)—C(10)	1.509	1.468	1.501	1.498
C(7)—C(8)	1.482	1.453	1.476	1.445
C(8)—C(9)	1.460	1.499	1.460	1.488
C(9)—C(10)	1.498	1.491	1.495	1.448
Angle		ω/deg		
M—C(1)—C(11)	82.30	85.71	88.98	93.92
M—C(11)—C(1)	62.76	60.20	64.09	54.48
M—C(6)—C(16)	—	—	—	91.14
M—C(16)—C(6)	—	—	—	56.16
M—C(9)—C(19)	—	84.37	—	—
M—C(19)—C(9)	—	61.00	—	—
M—C(10)—C(20)	—	—	87.33	—
M—C(20)—C(10)	—	—	59.04	—
α[b]	32.5	28.30	25.91	19.43
γ[c]	6.30	0.40	5.50	0.90
Total		$-E_{tot}$/au		
energy	871.7115	871.7266	871.6978	868.8798

[a] *Syn* and *anti* conformations of dication **5a** do not occur.

[b] The angle of deviation of the C(1)—C(11) bond from the plane of the Cp ring.

[c] The angle between the Cp* rings.

Therefore, in addition to the known procedure for the generation of homo- and heteroannular osmium dications **4a** and **5a** by the multistep method[3] and one-pot oxidation of osmocene **1a** in the $CF_3SO_3H—O_2$ system,[9] we developed new one-pot procedures for the synthesis of these dications by the reaction of **1a** with oleum in an inert atmosphere either with heating or upon irradiation.

Experimental

The ^1H NMR spectra of solutions of the neutral complexes in C_6D_6 were recorded on a Bruker AMX-400 spectrometer (400.13 MHz). For solutions of acids, C_6D_6 (98% D) was used as the external standard ($\delta_H(C_6D_5H)$ 7.25). The ^{13}C NMR spectra were measured on a Bruker AMX-400 spectrometer (100.61 MHz) with C_6D_6 as the external standard (δ_C 127.96). The mass spectra (EI) were obtained on an MS-890 instrument (70 eV, 150 °C, direct inlet of samples) in a C_6D_6 solution. Quantum-chemical calculations were carried out by the DFT method using the Becke—Lee—Yang—Parr functional (BLYP/LanL2DZ). Calculations were performed with full geometry optimization using the GAUSSIAN-98 program on a CRAY J-90 supercomputer (National Supercomputer Center, Oakland, California, USA). The *Z* matrices calculated earlier[14] for ruthenium analog **5b** were used as the initial approximation for the geometric parameters of the *gauche* and *anti* conformers of osmium dication **5a**.

Protonation and photolysis were carried out in NMR tubes filled with argon. Weighed samples of osmocene **1a** (~0.1 mmol), hydride **2a** (~0.1 mmol), or complex **3a** (0.02 mmol) as well as CF_3SO_3H (~3 mmol) or oleum (~0.6 g) were placed into tubes, and the tubes were sealed. UV photolysis was performed using an OKN-11 Hg lamp (850 W). The temperature of the experiments with irradiation was 35 °C. The ratios of the reaction products were calculated from the ratios of the integral intensities of the signals in the ^1H NMR spectra of the reaction mixtures.

Complexes **3a** ($An^- = BF_4^-$ or $CF_3CO_2^-$) were prepared[5] from $Cp^*OsC_5Me_4CH_2OH$ using HBF_4 etherate or CF_3CO_2H. Complex **2a** was synthesized according to a known procedure.[16]

The reactions were carried out with the use of CF_3SO_3H (Fluka, ≥98%) and freshly prepared 40% oleum. A calculated amount of H_2SO_4 (reagent grade) was added to SO_3 prepared by distillation of H_2SO_4 over P_2O_5.

Synthesis of the (η^5-pentamethylcyclopentadienyl)(η^5:σ:σ-trimethyl-1,2-dimethylenecyclopentadienyl)osmium dication (4a) and the bis(η^5:σ-tetramethylmethylenecyclopentadienyl)osmium dication (5a) and their alkoxylation to (η^5-pentamethylcyclopentadienyl)(η^5-trimethyl-1,2-dimethoxymethylcyclopentadienyl)osmium (10) and bis(η^5-tetramethylmethoxymethylcyclopentadienylosmium) (11). Osmocene **1a** (0.1168 g, 0.254 mmol) was placed into a two-neck flask and the flask was filled with argon. Then freshly prepared 40% oleum (8.11 g) was added with stirring using a magnetic stirrer at 50 °C for 3.5 h (control by ^1H NMR). A solution of sodium (1.5 g, 65.2 mmol) in anhydrous MeOH (20 mL) was added with stirring and cooling until the reaction mixture became alkaline. Then the reaction mixture was stirred at ~20 °C for 1 h and extracted with Et_2O. The ethereal extract was washed with water, dried over $MgSO_4$, and concentrated. An oily pale-yellow residue was obtained in a yield of 0.1031 g (78% of the theoretical value). According to the ^1H NMR spectroscopic data, the residue contained 42% of diether **10** and 58% of diether **11**. The yields of compounds **10** and **11** were 0.0433 g (0.083 mmol) and 0.060 g (0.115 mmol), respectively. For ^1H NMR spectra, see Table 5. ^{13}C NMR (C_6D_6), δ, **10:** 11.06 (β-Me), 11.37 (α-Me), 11.61 (γ-Me), 57.96 (OMe), 68.25 (OCH_2), 79.30, 79.60 (C_β, C_α), 80.01 (C_γ), 80.82 (C(1)); **11:** 11.20 (β-Me), 11.49 (α-Me), 58.23 (OMe), 68.75 (OCH_2), 78.93, 79.45, 80.63 (C_β, C_α, C(1)). MS, *m/z* (I_{rel} (%)): 522 $[M]^+$ (95), 491 [M – OMe] (63).

Synthesis of (η^5-pentamethylcyclopentadienyl)(η^5-tetramethylmethoxymethylcyclopentadienyl)osmium (12). Sodium (0.036 g, 1.57 mmol) was placed into a two-neck flask. Then anhydrous MeOH (2 mL) and hexane (15 mL) were added, after which a solution of complex **3a** ($An^- = CF_3CO_2^-$) (0.0285 g, 0.050 mmol) in MeOH (2 mL) was added with stirring. The reaction mixture was stirred at ~20 °C for 2.5 h. The upper organic layer was decanted. The residue of the solution was extracted with hexane. The combined hexane fractions were washed with water, dried over Na_2SO_4, and concentrated. Monoether **12** was obtained in a yield of 0.021 g (0.042 mmol; 85% of the theoretical value). Found (%): C, 51.32; H, 6.38; Os, 38.53. $C_{21}H_{32}OOs$. Calculated (%): C, 51.40; H, 6.57; Os, 38.76. For ^1H NMR, see Table 5. ^{13}C NMR (C_6D_6), δ: 10.31 (β-Me), 10.48 (α-Me), 10.73 (γ-Me), 57.15 (OMe), 68.04 (OCH_2), 77.42 (C(1)), 78.59 (γ-$\underline{C}$Me), 78.67 (2 $\underline{C}$Me), 79.22 (2 $\underline{C}$Me). MS, *m/z* (I_{rel} (%)): 492 $[M]^+$ (80), 462 $[M - 2 Me]^+$ (45).

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